Appendix G

Instrumentation and Platforms for Observations of Sea Surface pCO_2 and Related Properties

G.1 Introduction

Lack of data hinders progress in determining the spatial and temporal variability of surface pCO_2 and related biogeochemical tracers. Strategies are needed to increase spatial coverage and sampling frequency at reduced per datum cost. In this context, particular emphasis should be placed on the development of new sensor technology, particularly on instruments for measuring CO_2 and related quantities autonomously (Goyet *et al.*, 1992; DeGrandpre *et al.*, 1995; Friederich *et al.*, 1995; Tokar and Dickey, 2000; Varney, 2000). In particular, development should be encouraged for systems that can be interchangeably mounted on moorings and profiling floats or used as autonomous systems on volunteer observing ships (VOS). Infrastructure currently in place for other efforts such as buoys, drifters, commercial ships, and other ocean structures are prime platforms for sustained observations. Key physical parameters such as wind, salinity, and temperature are often already available from such platforms. Examples include the profiling PALACE and ARGO floats in the Atlantic and Pacific under the CLIVAR Program that currently provide T and S measurements (Davis *et al.*, 2000), the TOGA and PIRATA mooring array that provide wind, T, and current measurements, and the drifting buoy network that provides SST and sometimes pressure and wind. A combination of surface drifters, CO_2 sensors on profiling floats, and sensor arrays along mooring lines could provide a critical connection between surface and subsurface fields. In this section we describe some autonomous instruments and observing platforms that will allow us to study CO_2 and associated bioactive parameters.

G.2 Autonomous Sensors for Moorings, Drifters, Floats, and Volunteer Observing Ships

During recent years, a wide range of autonomous sensors have been developed and improved. A noninclusive list of sensors for chemical properties includes the following.

G.2.1 Sea surface pCO_2

Several autonomous and quasi-autonomous shipboard sensors have been developed by a variety of groups. One set is primarily based around LiCor infrared analyzers (Cooper *et al.*, 1998; Feely *et al.*, 1998; Wanninkhof and

Thoning, 1993). The surface water pCO_2 is determined by equilibrating surface water, pumped on board ship, with a headspace. The units commonly measure surface water and air mole fractions of CO_2. Standardization occurs by using compressed gas standards. Laboratory and shipboard intercomparison studies (Koertzinger *et al.*, 1999) have shown reasonable agreement between various units. It is thought that the major differences in results are caused by poorly calibrated thermometers, differences in compressed gas standards, and incomplete equilibration of the water flowing through the equilibrators. No commercial company currently builds a complete unit.

In situ sensors have been developed for moorings and drifters based either on an equilibrator design (Friederich *et al.*, 1995) or spectrophotometric analysis (DeGrandpre, 1995, 1999; Merlivat and Brault, 1995). In the latter design, CO_2 in seawater is equilibrated with a pH-sensitive dye across a gas-permeable membrane and the change in absorbance is measured with a small spectrophotometer. Three units, the SAMI, CARIOCA, and YSI (Yellow Springs Instruments) sensors are or will shortly be commercially available. The in situ sensors currently do not have any standards for calibration, although the IR-based unit is referenced against air.

G.2.2 pO_2

O_2 concentration measurements in the mixed layer reflect net production and gas fluxes over the O_2 residence time (typically 2 weeks). Values in the seasonal thermocline reflect net production since the onset of springtime stratification, because the thermocline is effectively capped off from the surface. O_2 can be measured continuously on moorings or along cruise tracks, thereby allowing one to collect extensive data sets that can be used to constrain biological fluxes in the upper ocean.

Several autonomous pO_2 analyzers are available for oceanographic use that can be installed on drifters, buoys, and VOS for oceanographic measurements. Rapid response units are used on CTDs. The in situ units currently available from Langdon Enterprises and YSI have an endurance of up to about 3 months without discernable drift under optimal conditions. As with the pCO_2 units, lack of calibration limits use in the fully autonomous mode. The fast response polarographic units installed on CTDs exhibit more drift on timescales of days to weeks.

G.2.3 Total dissolved gas pressure

Total dissolved gas pressure allows one to separate the contribution of physical and biological processes to dissolved O_2 supersaturation (Spitzer and Jenkins, 1989; Emerson *et al.*, 1991). The system is based on measuring the pressure under a gas-permeable membrane. An autonomous sensor is available through Pro-Oceanus Systems (McNeil *et al.*, 1995).

G.2.4 Autonomous NO_3^- and POC sensors

Euphotic zone concentrations of NO_3^- reflect seasonal net production as well as the restoration of nutrients by vertical mixing. POC concentrations give an important constraint on the fate of organic carbon produced in the mixed layer and the relationship between net and export production. Sensors for these properties now exist and have been successfully deployed on moorings (Johnson and Coletti, in preparation).

G.2.5 Other properties

Autonomous instruments can measure other relevant biogeochemical properties, including photosynthetically active radiation (PAR), spectral properties, and fluorescence. Automated water samplers permit sampling for trace metals and other properties. There are also, of course, autonomous instruments for measuring physical properties, including Acoustic Doppler Current Profilers, current meters, and temperature/salinity measuring devices.

G.2.6 Multiparameter sensors

A high-precision in situ instrument for TCO_2, pCO_2, TA, and pH is being developed by Robert Byrne and colleagues at the University of South Florida using a compact spectrophotometric analysis system (SEAS) (Byrne *et al.*, 2001). The system is capable of spectral analysis from 400 to 750 nm in both absorbance and fluorescence modes. The sample cell is configured to use long-pathlength liquid core wave guides (10–500 cm) for pH, pCO_2, total inorganic carbon, and total alkalinity. The system is deployed with the bottom-stationed ocean profiler (BSOP) or other similar profilers, but can be modified for just about any platform. These devices have been designed to carry SEAS sensors and other instruments, and telemeter chemical and physical data after each cycle.

G.3 Conclusions

In principle, all of these instruments can be deployed on ships and moorings, although a limited subset is likely to be more practical. Moorings permit long-term, continuous observations at selected locations. VOS allow chemical and biological properties to be measured over broad reaches of the oceans, but they sample the mixed layer only. Recently developed towed systems allow almost continuous depth profiling of many dissolved properties in the upper $\sim$100–200 m along cruise tracks of research ships, but at reduced speed.

Sensors on drifters, floats, and moorings add considerably to our ability to sample the oceans. Fewer properties can be measured, but it is possible to measure pCO_2 and other important properties, including T, S, NO_3^-, and O_2. Calibration and long-term stability remain significant issues for the long-term deployments advocated here.

G.4 References

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